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Catalytic Pyrolysis of Raw and Thermally Treated Cellulose Using Different Acidic Zeolites

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Abstract Fast pyrolysis of biomass using zeolite catalyst has shown to be effective in improving aromatic production. This study focuses on aromatic production through catalytic pyrolysis of major biomass constituent i.e., cellulose. Furthermore, cellulose was torrefied to understand torrefaction's effect on pyrolysis products. The influence of SiO_2/Al_2O_3 ratios of zeolite (ZSM-5) catalyst on aromatic production during pyrolysis of raw and torrefied cellulose was investigated. Results showed that the catalyst acidity played a pivotal role in eliminating anhydro sugars and other oxygenated compounds while producing more aromatics. The maximum aromatic yield (~25 wt%) was obtained when ZSM-5 with the highest acidity (SiO_2/Al_2O_3=30) was used, while the lowest yield (7.99 wt%) was obtained when the least acidic catalyst was used (SiO_2/Al_2O_3=280) for raw cellulose pyrolysis. Torrefaction process showed to have positive effect on the aromatic production from pyrolysis. There were no aromatics produced from pyrolysis of raw cellulose in the absence of catalyst, whereas significant amount of aromatic compounds were produced from both catalytic and noncatalytic pyrolyses of torrefied cellulose. The aromatic hydrocarbons produced from catalytic pyrolysis of torrefied cellulose were 5 % more than those produced from raw cellulose at the highest temperature and catalyst acidity (SiO_2/Al_2O_3=30).

Keywords Torrefaction · Cellulose · Zeolite · Acidity

Introduction

Biomass is considered as an excellent alternate energy source to help in meeting the world's fast growing energy demand. Renewable energy constitutes about 17 % of the total US energy consumption, and liquid biofuels account for almost 5 % of the renewable energy [1]. Among the different thermochemical and biochemical processes to convert biomass into biofuels, fast pyrolysis seems to be promising due to its high liquid yield. Although bio-oil can be used for production of transportation fuels, chemicals, and energy, bio-oil has certain properties that make it a poor fuel [2]. High water content in bio-oil results in low heating value which in turn results in poor thermal and chemical stability [3]. Moreover, its poor ignition and combustion properties make it difficult to be even cofired with coal or other conventional resources [4]. In spite of several differences in its properties compared to conventional fuels, it is considered to be a material that can be potentially used along with fossil-derived fuels to produce several useful products. However, in order to be used as an alternate transportation fuel, high oxygen content (~35 wt%) in bio-oil has to be reduced.

A number of studies are being focused on different upgrading techniques to improve the quality and stability of pyrolysis oil using different catalysts with or without the presence of high-pressure hydrogen [5–7]. Upgrading techniques focus on reduction or complete removal of oxygen present in the fuel, which otherwise makes it immiscible with current hydrocarbon fuel. At present, elimination of oxygen in biomass to some extent by thermal pretreatment process termed as "torrefaction" is gaining some attention. Torrefaction is a mild pyrolysis process that takes place at 200–300 °C in the absence of oxygen accompanied by

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changes in physical and chemical properties of the feedstock. Hemicellulose degradation, which occurs during torrefaction, can be considered as a major step resulting in the release of carbon monoxide and carbon dioxide along with formaldehyde, furfural, and other aldehydes [8, 9]. As a result, there is a decrease in oxygen and hydrogen content that causes relative increase of carbon. Also, due to the removal of hemicellulose during torrefaction, there is a reduction in mass by 20 to 30 %, but almost 90 % of the initial energy content is preserved and hence the energy density of torrefied biomass is higher than that of raw biomass and is closer to that of coal used for combustion purposes at severe torrefaction conditions [10–12]. In addition, torrefaction reduces grinding energy, which is potentially beneficial since fast pyrolysis process requires fine particles to produce high bio-oil yield [13].

However, before understanding the reaction mechanism of biomass and torrefied biomass pyrolysis, it is essential to study the pyrolytic behavior of the polysaccharides present in biomass extensively. Hemicellulose, cellulose, and lignin are the three main constituents of biomass and consist of approximately 25–35, 40–50, and 21–35 wt%, respectively. Cellulose is a linear polymer of glucose with β-1,4 linkages, which makes cellulose less flexible compared to hemicellulose [14]. It is both crystalline and amorphous with degree of polymerization around 10,000. Pyrolysis behavior of cellulose had been studied in the past, and few kinetic models have also been developed. One such model was a three-reaction model in which "active cellulose" (levoglucosan) formed by an "initiation reaction" undergoes parallel first order reactions to give char, volatiles, and gaseous products [15].

Several past studies have discussed fast pyrolysis of biomass constituents, especially cellulose [16–20]. Only limited studies [21, 22] are available on fast pyrolysis of torrefied biomass. However, none of them have focused on catalytic pyrolysis of torrefied cellulose. Therefore, the purpose of this study is to understand the influence of torrefaction, pyrolysis temperature, and catalyst acidity on the fast pyrolysis products of cellulose.

Experimental Setup

Cellulose Torrefaction

Pure cellulose, with a mean particle size between 50 and 350 μ, used in this study was purchased from Sigma Aldrich. It was then thermally pretreated (torrefied) at 225 °C for 30 min in a tubular furnace (Thermo Scientific model TF55035A-1), and vapors were purged using nitrogen stream flowing in at 20 mL/min. About 10 g of raw cellulose was torrefied in a stainless steel reactor (ID=0.35 in., OD=0.5 in., and 18 in. long). Thermogravimetric (TG) analysis of cellulose was performed using a TGA (PerkinElmer, model Pyris 1) to evaluate mass loss as a function of temperature with a heating rate of 10 °C/min and nitrogen flow rate of 15 mL/min. Ultimate analysis was performed for both raw and torrefied cellulose using a CHNS analyzer (PerkinElmer, model CHNS/O 2400 II) to measure carbon, hydrogen, nitrogen, and sulfur content. Moisture content of raw and torrefied cellulose was determined using ASTM standard (ASTM E871). Higher heating value of raw and torrefied cellulose was measured using an oxygen bomb calorimeter (IKA, model C 200). An FTIR analysis was done to study the structure of raw and torrefied cellulose using a PerkinElmer Spectrum model 400 (PerkinElmer Co., Waltham, MA). This equipment uses a single reflectance ATR diamond with a repeatable vertical pressure between samples to ensure repeatability in spectra acquisition between samples. For each sample, the spectrum was collected within 10 s by applying a vertical load on the sample. All scans were done at room temperature which was ~22 °C.

Fast Pyrolysis

Fast pyrolysis experiments were carried out using a commercial pyrolyzer (CDS Analytical Inc., model 5200). The probe had a computer-controlled heating element, which held a sample in a quartz tube. A reactant mixture (catalyst and cellulose) was packed between quartz wool in a quartz tube (25 mm long with 1.9 mm internal diameter). Catalytic fast pyrolysis was carried at three different temperatures (500, 550, and 600 °C) with four zeolite catalysts of different acidities (SiO_2/Al_2O_3=30, 50, 80, and 280) for both torrefied and raw cellulose. Catalyst to cellulose ratio was 1:4 and was kept constant for all the experiments. Temperature specified in pyroprobe experiments is the filament temperature, but the actual sample temperature in a pyroprobe can be 100–125 °C lower than the filament temperature. Four types of ZSM-5 catalyst (Zeolyst, Inc.) were received in ammonium cation form and were calcined in air at 550 °C for 2 h in a furnace to convert into H^+ZSM prior to use. Geometric mean particle size, silica to alumina ratio, and surface area of the four zeolites are given in Table 1.

Zeolite catalyst was physically mixed with cellulose or torrefied cellulose samples in 1:4 ratio. The biomass heating rate was kept constant at 2,000 °C/s throughout the study.

Table 1 Properties of different acidic zeolites

Silica to alumina (SiO_2/Al_2O_3) ratio	Geometric mean particle size (μm)	Surface area (m^2/g)
30 (Z30)	81.14	400
50 (Z50)	87.32	425
80 (Z80)	87.58	425
280 (Z280)	89.16	400

Helium gas was used as an inert pyrolysis gas as well as the carrier gas for the GC/MS system. A known amount of (approximately 1–3 mg) reactant mixture was taken for each run. The vapor from pyrolysis was carried to a trap maintained at 40 °C. The condensable vapor was adsorbed in the trap, whereas noncondensable vapor was purged using helium gas. The adsorbed compounds was then desorbed by heating the trap to 300 °C and carried to GC/MS for analysis using ultrahigh purity (99.999 %) helium purchased from Airgas Inc. The vapor transfer line from pyroprobe to GC/MS was maintained at 300 °C. Bio-oil compounds were analyzed with an Agilent 7890 GC/5975 MS using a DB 1701 column. The GC front inlet temperature was kept at 250 °C, and the GC oven was programmed with the following temperature regime: hold at 40 °C for 2 min, heated to 250 °C at 5 °C/min, and hold at 250 °C for 8 min. A split ratio of 50:1 was set for injection, and the gas flow rate was maintained at 1.25 mL/min. Compounds were identified using the National Institute of Standards and Technology (NIST) mass spectral library. Compounds that appeared consistently with high probability were selected and quantified. Quantification was done by injecting calibration standards into the GC/MS system. The slope of the calibration line was taken as the quantification factor in the calculation. Experiments were carried out in triplicates, and the average values are reported. The results are reported as carbon yield of each product group (aromatic hydrocarbons, furans, phenols, and anhydro sugars), which is calculated using Equation 1. The total carbon yield is the summation of carbon yield of each group such as aromatic hydrocarbons, furans, phenols, and anhydro sugars. In the case of torrefied biomass, it is the weight of torrefied biomass and carbon fraction of the torrefied biomass.

$$\text{Carbon yield (wt\%)} = \frac{\text{weight of each compound} \times \text{mass fraction of carbon in each compound}}{\text{weight of biomass} \times \text{mass fraction of carbon in biomass}} \times 100 \tag{1}$$

Statistical analyses were performed at 95 % confidence interval, and the data were analyzed using SAS 9.2 (Cary, North Carolina). One-way ANOVA (analysis of variance) analysis was performed to evaluate the effect of temperature and catalyst only on total carbon yield and carbon yield of aromatics.

Results

Effect of Torrefaction

Figure 1 shows thermogravimetric data of cellulose, and there was hardly any mass loss at the torrefaction temperature used in this study—less than 0.1 wt% (dry basis) of mass was lost at 225 °C. In addition, there were no significant changes in energy content and elemental composition.

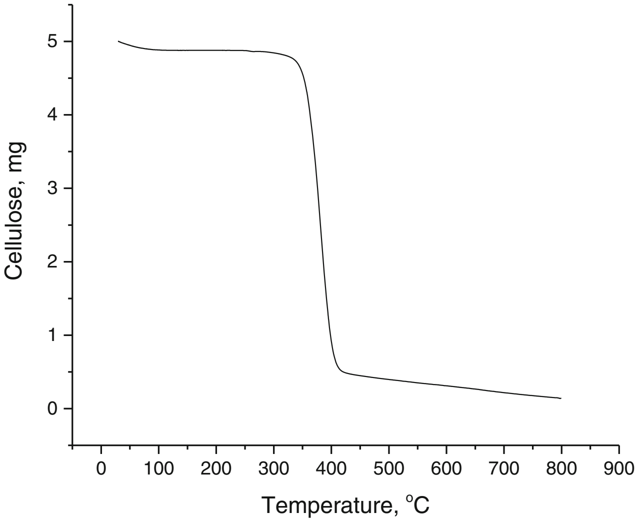


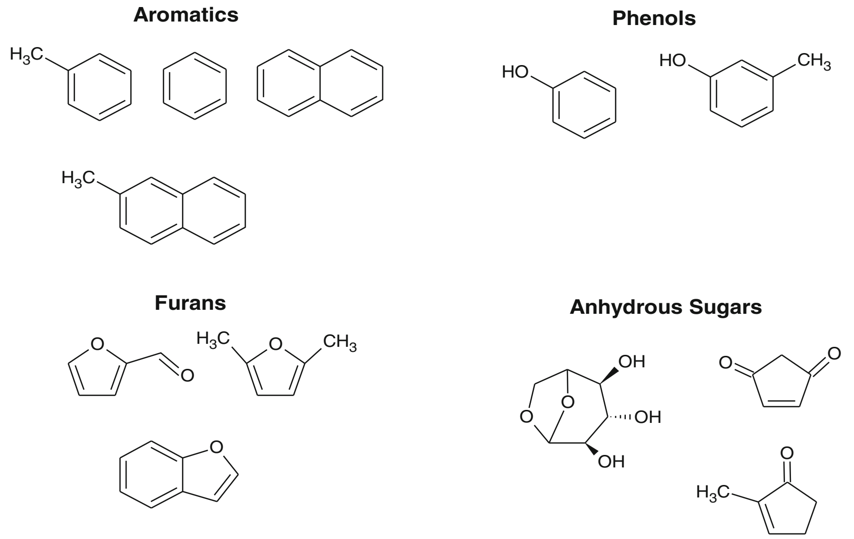
Fig. 1 Thermogravimetric profile of cellulose under nitrogen environment

Effect of Torrefaction: Carbon Yield

Products from GC/MS were grouped into four distinct groups: aromatics, phenols, furans, and anhydro sugars. The major compounds in each of these groups are shown in Fig. 2.

Figure 3 shows the effect of torrefaction on the product distribution from fast pyrolysis of cellulose at 600 °C. It can be observed that no phenolics, as expected, were observed from fast pyrolysis of both raw and torrefied cellulose. Anhydro sugar, mainly levoglucosan, was found to be a major product (~14 wt%) from fast pyrolysis of cellulose, while it was very minimal (~0.5 wt%) from the pyrolysis of torrefied cellulose. Pyrolysis of torrefied cellulose resulted in more of aromatics (~10 wt%), which was completely absent from raw cellulose pyrolysis. Hence, it can be assumed that thermal pretreatment modifies the structure of cellulose by altering the C–O–C and glycosidic bonds resulting in more aromatics during pyrolysis. An FTIR study was performed for raw and torrefied cellulose (Fig. 4), and the spectra collected from raw and torrefied cellulose were very similar with some differences such as peak around 1,040 cm^{-1} corresponds to aliphatic C–O–C and C–OH in alcohol and found to be declined for torrefied cellulose indicating dehydration along with the absent of hemiacetal bonds; peak around 1,230 cm^{-1} corresponds to CH_2–O–H deformation in cellulose and grew more in torrefied cellulose; and peak corresponds to weak carbonyl (C=O) stretch at ~1,730 cm^{-1} grew for torrefied cellulose [22–24]. Detailed understanding of structural changes in cellulose after torrefaction could require more advanced tools such as NMR.

Fig. 2 Major products of catalytic pyrolysis of raw and torrefied cellulose collected from GC/MS library



Catalytic Pyrolysis of Raw and Torrefied Cellulose

The effect of pyrolysis temperature on total carbon yield from catalytic pyrolysis of raw cellulose with four different acidic zeolites is depicted in Fig. 5. There was an increase in total carbon yield initially as the temperature increased from 500 to 550 °C; however, it either remained almost constant or showed a slight drop with further increase in temperature from 550 to 600 °C. This trend was same for all four zeolite catalysts. The total carbon yield of raw cellulose pyrolysis with Z30 was higher at all temperatures compared to that from Z50, Z80, and Z280. Statistical analysis (Tukey's test) was performed to study the significant differences between temperature and catalyst acidity on total carbon yield. From the results, it was found that temperature had significant effect (p value=0.0061) when the most acidic zeolite (Z30) was used. However, the temperature did not have significant effect when using other acidic zeolites (Z50, Z80, and Z280). With the use of Z30, the total carbon yields at high temperatures (550 and 600 °C) were significantly different as compared to lower temperature (500 °C). However, there was no significant difference found between the yields at 550 and 600 °C. Cellulose degrades at around 250–350 °C to produce primarily anhydro sugars like levoglucosan [14]. These compounds in the presence of catalyst can undergo series of reactions to get converted or broken down into several other carbon compounds. Although the reaction temperature enhances this conversion process, after reaching an optimum temperature, which in our study was found to be 550 °C, there was no major increase in carbon yield with further increase in temperature, and this is clearly seen from the results presented in Fig. 5. Similarly, catalyst type (p value=0.0763) did not have significant effect on total carbon yield at 500 °C, whereas the total carbon yield was different with all the catalyst type (p value=0.0001) at 600 °C. At 550 °C, there was no significant difference on total carbon yield with Z50 and Z80. It is clear that the Z30 favored high total carbon yield with raw cellulose pyrolysis.

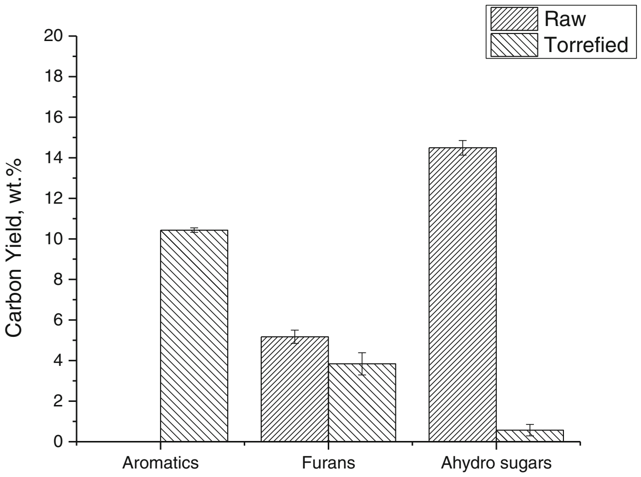
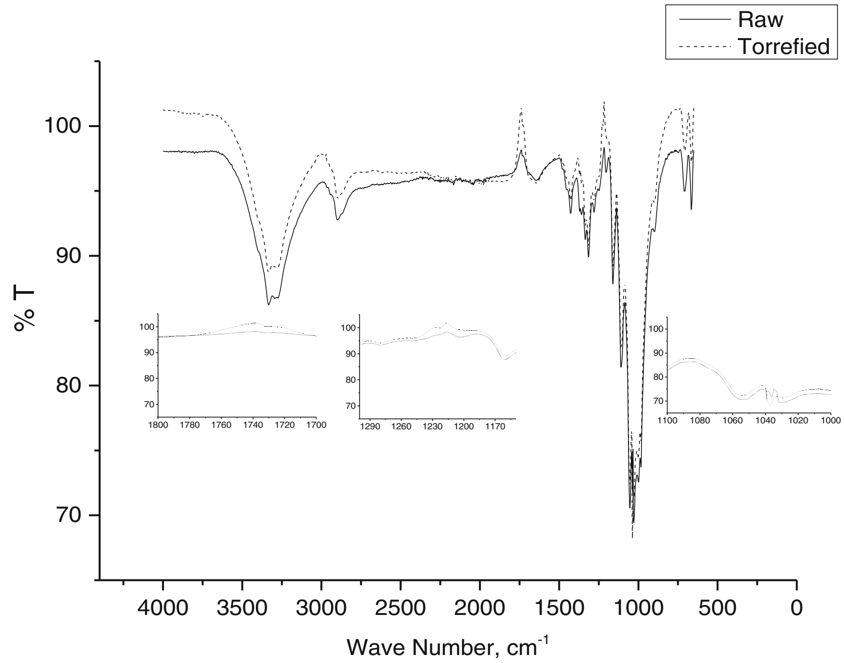


Fig. 3 Effect of torrefaction on the product distribution from the noncatalytic fast pyrolysis of cellulose at 600 °C

The effect of temperature on total carbon yield from catalytic pyrolysis of torrefied cellulose is given in Fig. 6. From the figure, it can be observed that total carbon yield increased as temperature increased from 500 to 550 °C. The maximum yield (~39.5 %) was obtained at 550 °C with the use of Z30. With further increase in temperature from 550 to 600 °C, the carbon yield remains constant when more acidic catalysts (Z30 and Z50) were used and showed a sudden drop when low acidic catalysts (Z80 and Z280) were used. The lowest yield (~5.9 %) was produced at 600 °C with the use of the least acidic ZSM-5 catalyst (Z280). Under the same conditions, catalytic pyrolysis of raw cellulose produced more total carbon yields (~16.94 %) compared to that of torrefied cellulose even with the use of the least acidic ZSM-5 catalyst. In

Fig. 4 FTIR spectra for raw and torrefied cellulose



general, raw cellulose pyrolysis gave more total carbon yield as compared to torrefied cellulose pyrolysis. Based on Tukey's test, temperature had significant effect with the use of Z30 (*p* value=0.0023), Z80 (*p* value=0.0084), and Z280 (*p* value=0.0299). However, temperature did not have significant effect with the use of Z50 (*p* value=0.7374). Total carbon yield at 500 °C was significantly different than that at 550 and 600 °C using Z30. However, the total carbon yield at 550 and 600 °C was not significantly different from each other. When low acidic zeolites (Z80 and Z280) were used, the total carbon yields at temperatures 500 and 550 °C were significantly different as compared to the yield at 600 °C. Among the total carbon yield obtained using different acidic zeolites, only the yields obtained with the use of zeolite with Z50 and Z80 were not significantly different at 500 °C (*p* value=0.0022). However, at 550 (*p* value=0.0002) and 600 °C (*p* value=<0.001), the total carbon yields obtained from all acidic zeolites were significantly different from one another.

Figure 7 shows the effect of pyrolysis temperature and catalyst acidity on the product distribution of catalytic pyrolysis of raw cellulose. Aromatic yield increased with temperature for all catalyst types; however, big increase was seen only when the temperature was increased from 500 to 550 °C. Raw cellulose pyrolysis gave high yield of aromatics (~25 wt%) with the use of the most acidic zeolite (Z30) compared to less acidic zeolites (Z80 and Z280). Use of Z50 also produced

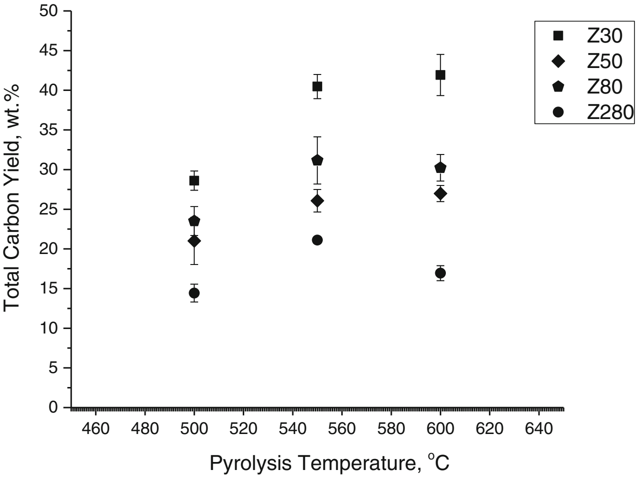


Fig. 5 Effect of pyrolysis temperature on total carbon yield from the catalytic pyrolysis of raw cellulose with three different acidic zeolites (catalyst to cellulose ratio=1:4)

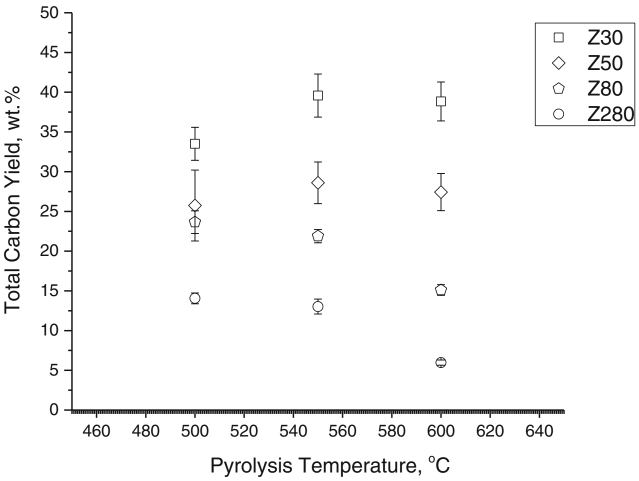


Fig. 6 Effect of pyrolysis temperature on total carbon yield from catalytic pyrolysis of torrefied cellulose

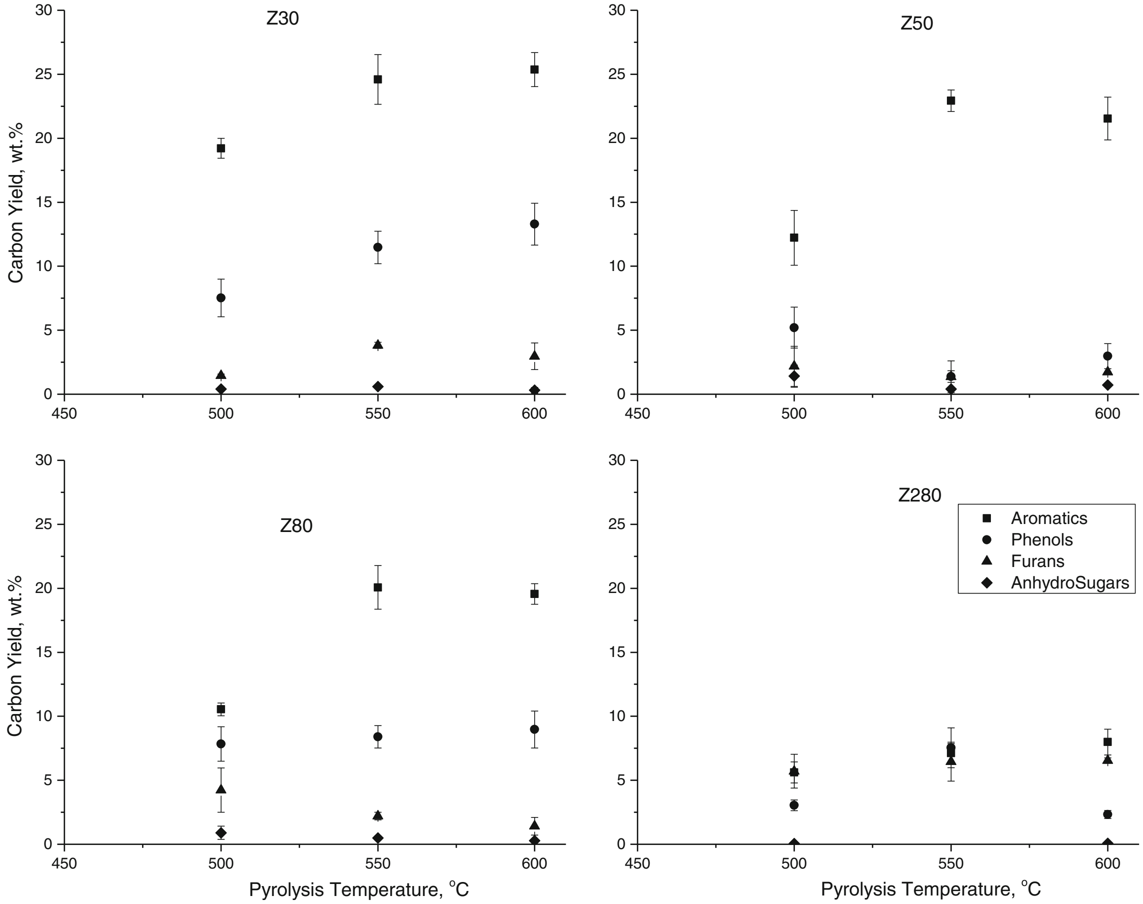


Fig. 7 Effect of pyrolysis temperature and catalyst acidity on the product distribution from catalytic pyrolysis of raw cellulose

more aromatics which accounted for ~20 wt% carbon. Furans and its derivatives were found to be less with the use of the most acidic catalyst, ZSM30. This could be due to the fact that more acidic catalyst exhibited good cracking ability and produced more aromatics as a result [25]. In addition, presence of catalyst helped in minimizing anhydro sugar yield from pyrolysis of raw cellulose. Results from the Tukey's test showed that for raw cellulose pyrolysis, except with the use of the most (Z30; *p* value=0.3265) and least acidic (Z280; *p* value= 0.0417) zeolites, other two acidic zeolites (Z50; *p* value= 0.037 and Z80; *p* value=0.0159) showed significant difference on the aromatic yield with temperature. With the use of acidic zeolites (Z50 and Z80), the yield at 500 °C was significantly different from the yield at 550 and 600 °C. However, no significant difference was observed between the yield at 550 and 600 °C. Results from the Tukey's test for the effect of catalyst acidity on aromatic yield showed that at 500 °C (*p* value=0.0024), the aromatic yields with the use of Z30 and Z50 were significantly different than from those of Z80 and Z280. At 550 and 600 °C, the yields obtained with the use of zeolites (Z30, Z50, and Z80) were significantly different only from the yield obtained with Z280.

Effect of temperature and catalyst acidity on product distribution from the catalytic pyrolysis of torrefied cellulose is given in Fig. 8. It can be seen from the figure that both temperature and ZSM-5 acidity had a positive effect on aromatic yield from the catalytic pyrolysis of torrefied cellulose. Aromatics, which included substituted benzene and naphthalene, were produced more at the highest temperature and catalyst acidity (maximum yield=30.91 wt% at 600 °C with Z30). This yield was much higher than that produced from catalytic pyrolysis of raw cellulose (~25 wt%) at the same conditions. However, other groups such as phenols and furans were found relatively more from catalytic pyrolysis of raw cellulose than that of torrefied cellulose at all three temperatures and four ZSM-5 acidities. Hence, it could be interpreted that along with the effect of catalyst acidity, the thermal pretreatment process also enhances hydrocarbon aromatic production. Results from the Tukey's test showed that the use of high acidic zeolites (Z30 and Z50) at 500 °C resulted in the aromatic yield significantly different from 550 and 600 °C; however, the yields at 550 and 600 °C were not significantly different from each other. The use of low acidic zeolites (Z80 and Z280) at 600 °C resulted in aromatic yield

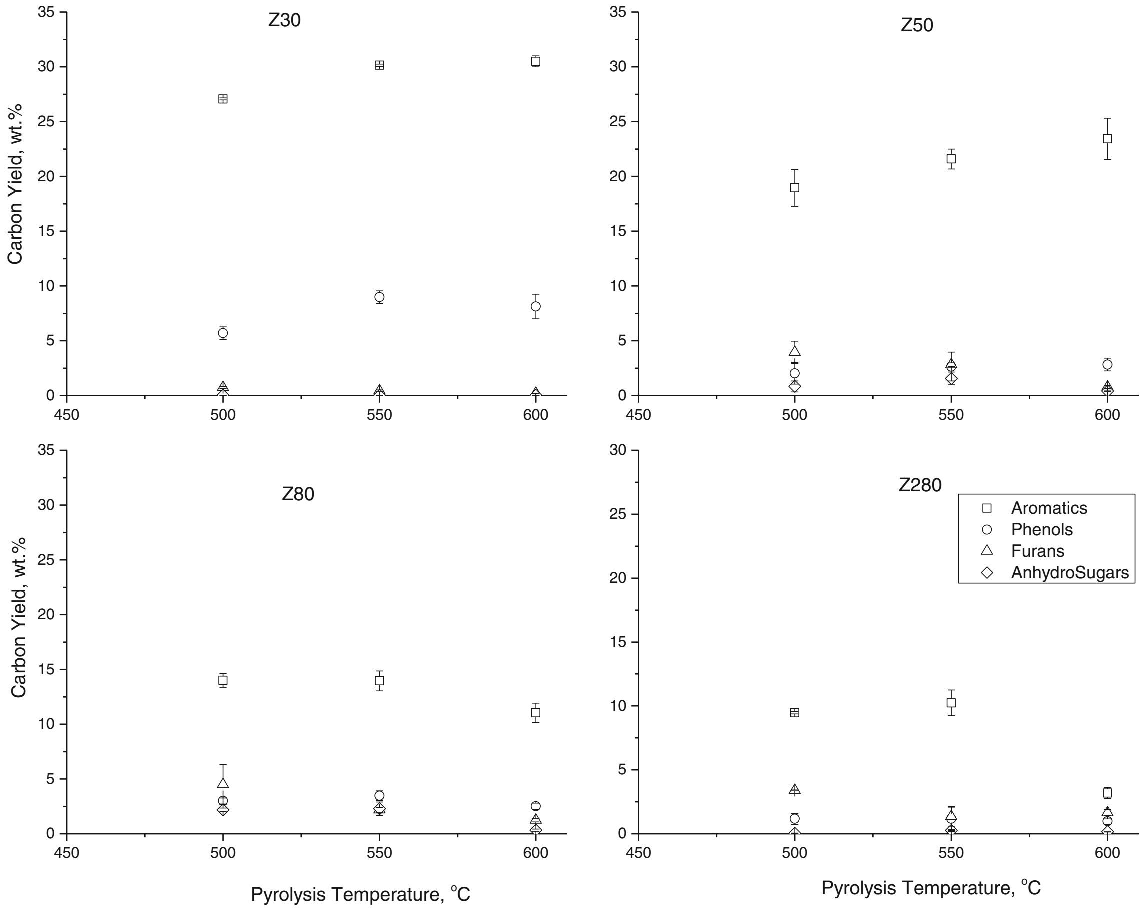


Fig. 8 Effect of pyrolysis temperature and catalyst acidity on the product distribution from catalytic pyrolysis of torrefied cellulose

significantly different from 500 and 550 °C; however, the yields at 500 and 550 °C were not significantly different from each other. However, aromatic yields with four acidic zeolites were significantly different from each other at all temperatures.

Catalyst Chemistry and Acidity

Several researchers [16, 25, 26] have proposed various reaction mechanisms on the catalytic conversion of carbohydrates into aromatics or hydrocarbon pool. Mihalcik et al. [25] gave a three-step pathway for deoxygenation of oxygenated organics: dehydration, decarboxylation, and decarbonylation. In addition, the study also concluded that since pyrolysis of cellulose with ZSM-5 resulted in more of CO_2, dehydration and decarboxylation reactions were more active. Carlson et al. [26] concluded that pyrolysis process involves homogenous thermal decomposition reaction that results in small oxygenates, which further undergoes acid catalyzed dehydration, decarboxylation, and decarbonylation reactions to form olefins, which later combines to produce aromatics. In another study of Huber and his coworkers [16], a two-step mechanism for catalytic fast pyrolysis of glucose was proposed. In the first step, glucose is decomposed into small oxygenates (mainly anhydro sugars) through retro-aldol, grob fragmentation, and dehydration reactions followed by the conversion of dehydrated products to aromatics in the catalyst pore in the second step. Results from our current study also show that primary product from noncatalytic pyrolysis of raw cellulose is levoglucosan, and this anhydro sugar is completely eliminated when catalyst is used. Hence, catalyst provides a platform for selectively converting the anhydro sugars into aromatic hydrocarbons. Also, the products from catalytic pyrolysis of cellulose show that aromatic yield increases as the catalyst acidity decreases. The maximum yield (~25 %) was found with the use of catalyst having the highest acidity (Z30) at 600 °C. Therefore, it could be concluded that high catalyst acidity or low SiO_2/Al_2O_3 ratio increases the ability of catalyst to perform cracking reactions in case of raw cellulose pyrolysis. An overall mechanism that can be drawn from all of the above mechanisms and our results is that pyrolysis of raw cellulose results in small oxygenates—primarily levoglucosan and few furans. Presence of catalyst enables selective elimination or conversion of these oxygenates into aromatics through dehydration, decarboxylation, and decarbonylation reactions. Although several studies have been carried out for catalytic pyrolysis of raw cellulose, no research work has reported the effect of catalyst chemistry on torrefied cellulose pyrolysis.

Reaction Mechanism

Figure 9 shows the reaction mechanism for the pyrolysis of raw and torrefied cellulose. The reaction mechanism of raw cellulose shown in Fig. 9 is documented elsewhere [27]. According to Lu et al. [27], during pyrolysis of raw cellulose, the glycosidic bonds, which form the backbone of cellulose, are broken resulting in several reducing sugars. Anhydro sugar mainly levoglucosan is formed through a series of protonation and deprotonation reactions. However, it is impossible to completely break the glycosidic bonds during short pyrolysis processes, and hence along with levoglucosan, several anhydro oligosaccharides with different degrees of polymerization will be formed. The cleavage of glycosidic bonds is accelerated at higher temperatures, which results in higher levoglucosan yield at higher pyrolysis temperatures. A reaction mechanism for pyrolysis of torrefied cellulose was proposed based on our observation. As previously discussed, more aromatics and very less anhydro sugars were produced from pyrolysis of torrefied cellulose. This indicated that torrefaction could cause changes in cellulose structure. Based on our observation and open literature, it was concluded that torrefaction results in differences in several bonds such as C–O–C, C–O–H, and CH_2–OH. It can be hypothesized that during torrefaction, certain bonds change in the cellulose along with glycosidic bond breakage that results in an open chain structure during pyrolysis as well. Torrefaction changes cellulose structure (depolymerization, decrystalization, condensation), and it is possible that these changes in torrefaction could push "ring-opening" during pyrolysis, comparing to the pyrolysis with nontorrefied cellulose. During pyrolysis, the open chain structure undergoes several dehydration, decarbonylation, and aromatization reactions to form olefins, BTX (benzene, toluene, and xylene) and furans as primary products.

Conclusion

Catalytic fast pyrolysis was carried out on raw and torrefied cellulose with zeolite catalysts of varying acidity. It was

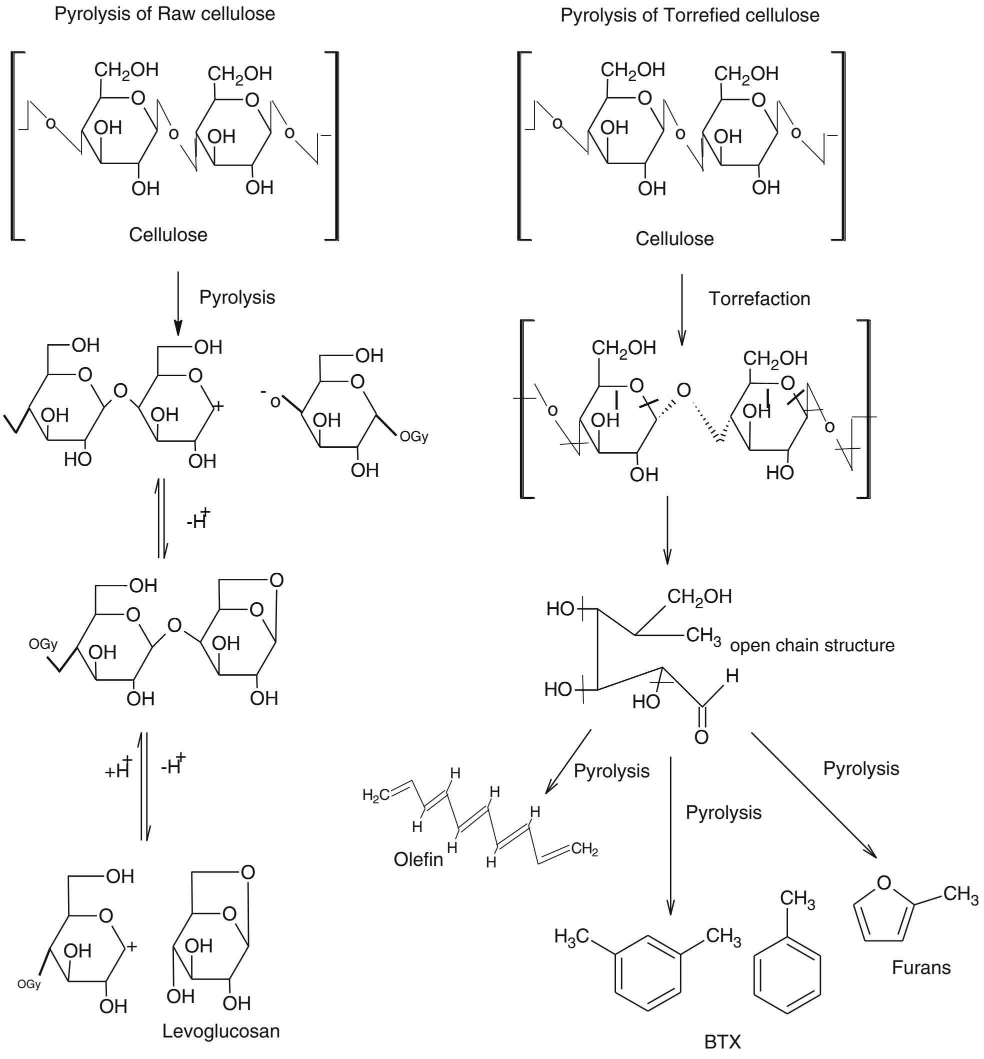


Fig. 9 Proposed reaction mechanism for non catalytic pyrolysis of raw and torrefied cellulose

concluded from the results that catalyst acidity, pyrolysis temperature, and torrefaction enhanced the production of aromatics from fast pyrolysis of cellulose. It was observed that anhydro sugars (levoglucosan) which accounted for ~14 wt% from the pyrolysis of raw cellulose were found very minimal from the pyrolysis of torrefied cellulose. Similarly, aromatics was ~10 wt% from pyrolysis of torrefied cellulose while it was completely absent from pyrolysis of raw cellulose, which indicated that torrefaction probably resulted in structural changes in cellulose and produced aromatic hydrocarbons. It is hypothesized that as a result of torrefaction, glycosidic bonds are partially cleaved resulting in an open chain structure which undergoes dehydration, decarbonylation, and aromatization reactions to produce aromatics as primary products. Results from catalytic pyrolysis of raw and torrefied cellulose showed that catalyst acidity played a pivotal role in eliminating oxygenates and promoting aromatic production. Maximum yield of aromatics was obtained when ZSM-5 with the highest acidity (SiO_2/Al_2O_3=30) was used for both torrefied and raw cellulose. However, torrefaction did not increase total carbon yield. For catalytic pyrolysis of torrefied and raw cellulose, the total carbon yield increased with increase in temperature until 550 °C after which it either remained constant or showed a slight drop.

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